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Structure and Reactions of Cuprous Thiobenzoate

Cuprous thiobenzoate is capable of displacing I^- from aliphatic and activated aromatic iodides, in alcoholic or alcohol–pyridine solution, with formation of thiolbenzoates in excellent yield. The reaction fails with other halogenated substrates. In these cases, the products of prolonged heating of the reaction mixture are ethyl benzoate, dibenzoyl disulfide, benzoic acid, thiobenzoic acid, hydrogen sulfide, and cuprous sulfide.

Le benzoate de cuivre(I) est capable de déplacer I^- des iodures aromatiques activés et aliphatiques, en solution alcoolique ou de alcool–pyridine, avec la formation de thiolbenzoates avec un excellent rendement. La réaction ne procéde pas avec autres substrats halogénés. Dans ces cas les produits de chauffage prolongé du mélange de réaction sont le benzoate d'éthyle, le bisulfure de benzoyle, l'acide benzoïque, l'acide thiobenzoïque, acide sulfhydrique et le sulfure de cuivre(I).

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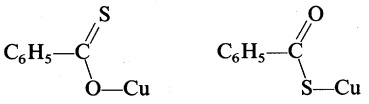
Introduction

In a recent article Nair and Nair (1) concluded, chiefly on the basis of infrared measurements, that in cuprous thiobenzoate, copper is linked to the oxygen, rather than to the sulfur, as in **1**. This article prompted an investigation



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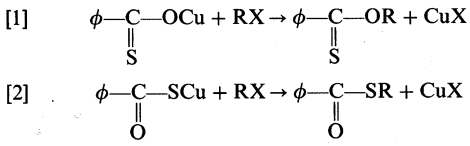

ϕ = phenyl; R = alkyl or aryl; X = halogen

able methods for thionesters are indirect (2, 3). If, however, **2** should prove to be the correct structure of cuprous thiobenzoate, thiolbenzoate esters should result instead, according to reaction 2. Since thiolesters, by acid or alkaline hydrolysis, always yield a carboxylic acid and a thiol (2), the formation of thiolbenzoates with cuprous thiobenzoate would afford a simple two-step method for the synthesis of aromatic and aliphatic thiols and polythiols starting from the corresponding halides.

Results and Discussion

The reaction of cuprous thiobenzoate with the following organic halides has been studied: bromobenzene, fluorobenzene, *p*-iodotoluene, *p*-chlorobenzoic acid, *o*-iodobenzoic acid, iodomethane, 1,2-dichlorotetrafluorocyclobut-1-ene, 1-bromopropane, and 2-chloroethanol. Apparently, cuprous thiobenzoate is not as versatile as cuprous thiophenolate and aliphatic mercaptides (4, 5) in displacing halogens from organic substrates. In fact, only *o*-iodobenzoic acid and iodomethane reacted. However, thiolbenzoates were obtained rather than thionbenzoates.

Iodomethane failed to react in alcohol at reflux temperature. However, when two molar equivalents of pyridine per mole of cuprous thiobenzoate was added, methyl thiolbenzoate formed with 90% yield. Its infrared and mass spectra are identical with those of an authentic sample of *S*-methyl thiobenzoate prepared from benzoyl chloride and methyl mercaptan. When one half molar equivalent of pyridine was used, the yield dropped to 50%. In both cases a small amount of ethyl benzoate was present in the crude product.

The reaction of *o*-iodobenzoic acid with cuprous thiobenzoate proceeded smoothly and quantitatively in absence of pyridine with formation of a thioester. Its infrared spectrum shows a band at 1682 cm^{-1} ($\nu C{=}O$) consistent with a thiolbenzoate structure (6). The high-resolution mass spectrum of the thioester (molecular ion at *m/e* 258, elemental composition $C_{14}H_{10}O_3S$) has the base peak at *m/e* 105 ($C_7H_5O^+$), and shows two intense rearrangement ions at *m/e* 122 ($C_7H_6O_2^{+\cdot}$) and *m/e* 136 ($C_7H_4OS^{+\cdot}$). These fragments are consistent with a thiolbenzoate structure only. Chemical confirmation was obtained by alkaline hydrolysis which afforded benzoic acid and diphenyl disulfide 2,2′-dicarboxylic acid (after $FeCl_3$ oxidation).

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The formation of thiolesters, instead of the thionesters one would expect on the basis of Nair and Nair's conclusion (1), does not necessarily settle the problem of the structure of the salt. The formation of *S*-thiobenzoates can be explained if one admits the existence of an equilibrium mixture of the two tautomeric forms **1** and **2**, the latter reacting much faster than the former (3).

The behavior of cuprous thiobenzoate is somewhat reminiscent of that of cuprous benzylmercaptide, *t*-butylmercaptide, and xanthate (5); namely, with certain substrates it decomposes before the reaction temperature is reached. Unlike cuprous benzylmercaptide (7), the thiobenzoate fails to react with 1,2-dichlorotetra-

fluorocyclobut-1-ene, even in the presence of pyridine.

On the basis of the above experiments, it appears that cuprous thiobenzoate has a good potential for the synthesis of *S*-thioesters from halides. However, its usefulness is limited to the reaction with aliphatic and activated aromatic iodides.

Experimental

General Conditions

The i.r. spectra were recorded on a Beckman IR 5A instrument, and were calibrated with polystyrene. The mass spectra were determined on a CEC 21-110B double-focusing spectrometer (ionizing energy 70 eV). Accurate mass measurements were made by the peak-matching method using a perfluorokerosene reference. Gas-liquid chromatographic separations were performed with a 240 cm × 6 mm column packed with Chromosorb W coated with 20% Silicone SE-30, and with a 420 cm × 6 mm column packed with Chromosorb W coated with 15% Triton X305. The instrument was a 5750 Hewlett–Packard equipped with a thermal conductivity cell. The reactions were carried out in alcohol or alcohol–pyridine.

Methyl Thiolbenzoate

Two grams (0.01 mol) of cuprous thiobenzoate was suspended in 20 ml of ethanol and 1.6 ml (0.02 mol) of pyridine, and the mixture was heated to mild reflux. Methyl iodide (3.55 g, 0.025 mol) was added, and heating continued for 45 min with magnetic stirring. The reaction mixture was then poured into ice-water containing 2 ml of concentrated hydrochloric acid, and extracted with chloroform. After drying, evaporation of the solvent afforded 1.44 g of crude methyl thiolbenzoate which was contaminated with 5% of ethyl benzoate, as calculated by peak area measurement of the gas chromatogram. Therefore, the actual yield was 90%.

2-(Benzoylthiol)benzoic Acid

Two grams (0.01 mol) of cuprous thiobenzoate and 2.48 g (0.01 mol) of *o*-iodobenzoic acid were heated at gentle reflux in 20 ml of ethanol for 90 min with stirring. The color of the suspended solid changed from brick-red to tan in 45 min. No pyridine was added as the change in color was indicative of reaction. An excess of alcohol was added, and the suspension was filtered hot through a 2 cm layer of Celite 245. The crude material (2.50 g) was recrystallized from ethanol; m.p. 160–161° (Fisher–Johns, uncorrected). This compound has not been previously reported in the literature. Its i.r. spectrum (Nujol) shows bands at 2500 ~ 2800(w), 1698(sh), 1682(s), 1585(m), 1418(m), 1316(m), 1292(w), 1212(m), 1185(m), 1152(w), 1059(w), 963(w), 910(s), 800(m), 772(m), 748(s), 697(m), 687(s), 648(w), 639(m) cm^{-1}. In the mass spectrum, the ten most intense peaks (*m/e*) are (percentage of the base peak and elemental composition in parentheses): 50(9%, $C_4H_2^{+\cdot}$), 51(21%, $C_4H_3^+$), 77(57%, $C_6H_5^+$), 105(100%, $C_7H_5O^+$), 106(9%, $C_6{}^{13}CH_5O^+$), 108(9%, $C_6H_4S^{+\cdot}$), 122(18%, $C_7H_6O_2^{+\cdot}$), 136(37%, $C_7H_4OS^{+\cdot}$), 153(3%, $C_7H_5O_2S^+$), 258(3%, $C_{14}H_{10}O_3S^{+\cdot}$). All the above elemental compositions are the result of accurate mass measurements.

The author thanks Dr. John M. Ruth, Entomology Research Division, A.R.S., U.S. Department of Agriculture, Beltsville, Maryland, for the mass spectral measurements, and Mr. Vincent P. Flanagan of this laboratory for the gas–liquid chromatographic separations.

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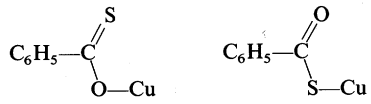

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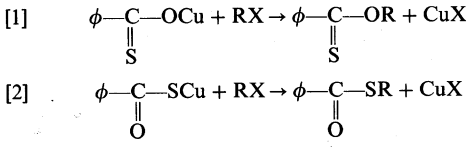

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